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Aqueous/ionic liquid interfacial polymerization for preparing polyaniline nanoparticles

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Abstract

The interfacial polymerization of aniline at aqueous/IL has been conducted. The product was characterized by transmission electron microscope (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV–vis spectroscopy, thermal gravimetric analysis (GTA), and electrical conductivity measurement. In this route, both solvents used are environmentally benign and polyaniline (PANI) particles with diameters from about 30–80 nm can be fabricated. We believe that this method can be used to synthesize some other useful polymers.

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Keywords: Ionic liquid; Interfacial polymerization; Polyaniline

1. Introduction

Interfacial polymerization (IP) involves step polymerization of two reactive monomers or agents, which are dissolved respectively in two immiscible phases and the reaction takes place at the interface of the two liquids [1]. IP has been used to prepare various polymers, such as poly(urea) [2], poly(amide), and poly(ester) capsules [3]. It allows the synthesis of polymers at low temperature with limited side reactions, and can avoid the use of catalysts or phase transfer agents [4]. The relative ease of IP has made it the preferred technique in many fields, ranging from microencapsulation of pharmaceutical products [5] to preparing conducting polymers [6]. IP is commonly done with volatile organic solvents as the organic phase, such as benzene [7], chloroform [8], toluene [9]. Recently, polyaniline (PANI) [10] was synthesized at the water/organic solvent interface by IP using carbon tetrachloride, benzene, toluene, or CS_2 as the organic solvents and high quality nanofibers could be fabricated [11].

Room temperature ionic liquids (ILs), which are organic salts and are liquids at room temperature, have attracted much attention as promising green solvents [12]. The nonvolatile nature of ILs gives them significant advantage in minimizing solvent consumption. They are good solvents for organic, inorganic, and polymeric compounds, and have been used as media for chemical reactions [12b], including polymerization [13] and IL/CO_2 biphasic reactions and separation [14], liquid–liquid extraction [15] and pervaporation [14b,16].

PANI is one of the most promising conducting polymers with various applications [17]. It is known that the processability of PANI is rather poor because it is infusible and insoluble in common solvents. One of the approaches to improve its processability is preparing nano-sized particles. Up to now, different methods [18] have been used to synthesize PANI nanoparticles, such as oxidative polymerization of aniline in the presence of micelles [19], a steric stabilizer [20], colloidal silica particles [21], or in reverse microemulsion [22], and pulsed potentiostatic method has also been applied to prepare the PANI nanoparticles [23].

Both water and ILs are environmental benign solvents. In this work, we carried out the first work to carry out IP at the aqueous/IL interface, and PANI nanoparticles with diameters of 30–80 nm were synthesized based on chemical oxidative polymerization of aniline using potassium peroxydisulfate as the oxidant [24]. We believe that this route can also be used to prepare other useful polymers with some potential advantages.

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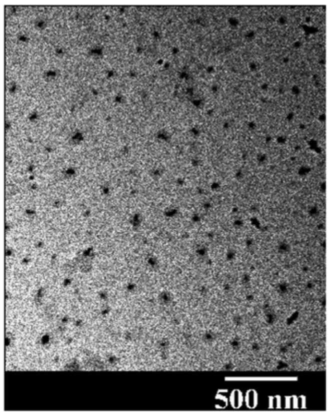

Fig. 1. TEM micrograph of PANI nanoparticles.

2. Experimental

2.1. Materials

1-Butyl-3-methylimidazolium hexafluorophosphate ([C_4mim] PF_6) was synthesized according to the procedures reported in the literature [25]. Aniline was distilled twice under atmospheric pressure and stored in dark at low temperature prior to use. Hydrochloric acid and other reagents were used without further purification. All aqueous solutions were prepared using distilled water.

In a typical synthesis, 0.5 g of aniline was dissolved in 10 mL of IL, while Potassium peroxydisulfate was dissolved in water with hydrochloric acid (1 M HCl). The two solutions were then carefully transferred to a beaker, generating an interface between the two layers. After 3–5 min, green PANI formed at the interface and then gradually diffused into the aqueous phase. After 24 h, the entire water phase was filled homogeneously with dark-green PANI, while the IL layer showed a color of orange, likely due to the formation of aniline oligomers. The aqueous phase was then collected, and the residue was collected in a Buchner funnel and washed with ethanol and water to remove the unreacted chemicals and aniline oligomers. The obtained PANI cakes were dried in a vacuum oven at 40 °C for 36 h. The synthetic yield was 25%.

2.2. Characterization

The morphology of the synthesized PANI was examined by a Jeol-2010 transmission electron microscope (TEM) operated at 200 kV. X-ray diffraction experiments were carried out on a D/MAX.RB model X-ray diffractometer with Cu K_λ radiation. Fourier transform infrared (FTIR) spectra were recorded with a Tensor 27 (Bruker). UV–vis spectra of PANI dissolved in *m*-cresol were recorded with a TU-1201 spectrophotometer (Beijing General Instrument Factory). Thermal gravimetric analysis of the HCl doped PANI was carried out with Perkin–Elmer TDA-7 at the heating rate of 20 °C/min up to 700 °C in N_2 atmosphere. The electrical conductivity of compressed pellets at room temperature was measured by a standard four-probe method using a Keithley 196 System DMM digital multimeter and an Advantest R1642 programmable DC voltage/current generator as the current source.

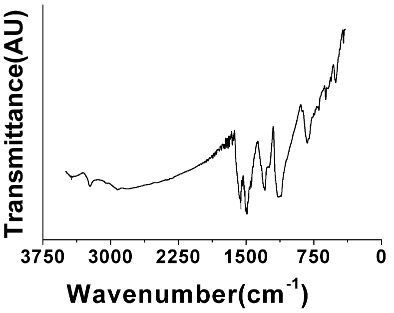

Fig. 2. FTIR spectra of HCl doped PANI.

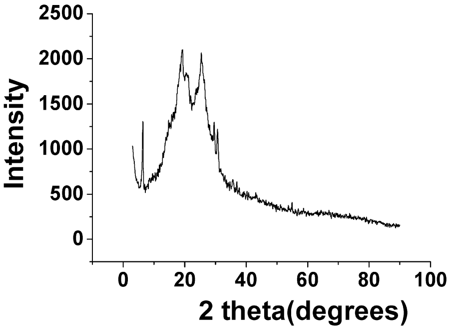

Fig. 3. X-ray diffraction patterns of PANI.

3. Results and discussion

Fig. 1 shows the TEM micrograph of the resulting PANI particles, which clearly shows the formation of PANI particles in a range from about 30–80 nm. The morphology is different from that synthesized in organic solvents/water IP, which yielded nanofibers [11]. The mechanism of the formation of the PANI nanoparticles is under studying.

The FTIR spectrum of the PANI (Fig. 2) is in good agreement with previously reported results [26]. For instance, the large descending base line in the spectral region 4000–2000 cm^{-1} has been attributed to free-electron conduction in the doped polymer [27]. The main peaks at 1556.2 and 1489.7 cm^{-1} correspond to stretching deformations of quinone and benzene rings, respectively. The bands at 1293.3, 1142.1, and 821.1 cm^{-1} can be assigned to

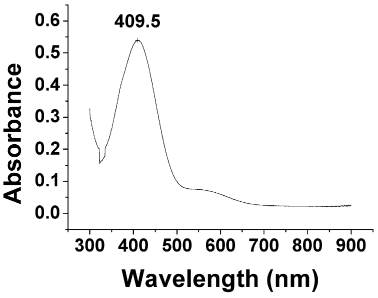

Fig. 4. UV–vis spectrum of the PANI.

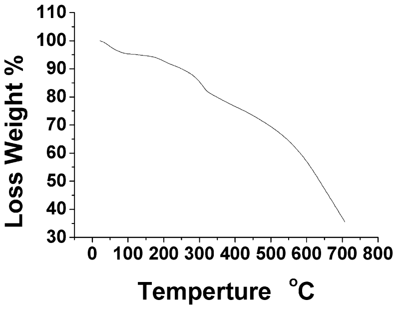

Fig. 5. TGA curves of PANI.

C–N stretch in a secondary aromatic amine, the aromatic C–H in-plane bending modes, and the out of plane deformations of C–H in the 1,4-disubstituted benzene ring, respectively.

Fig. 3 shows the X-ray diffraction patterns of the sample. Two broad peaks centered at $2\theta = 19°$ and 25° can be observed, which are ascribed to the periodicity parallel and perpendicular to the polymer chain [28], respectively. In the XRD patterns, no peaks of low-molecular-weight crystalline compounds are observed.

The UV–vis spectrum of the PANI is shown in Fig. 4. An absorption peak at 409.5 nm can be assigned to the localized polarons which are the characteristic of the protonated PANI [29].

Fig. 5 shows the TGA thermograph of the PANI powders. The initial mass loss between 50–150 °C is mainly due to the release of moisture and dopant (HCl) from the surface of PANI. Further mass loss of PANI that takes place at a slower rate up to 300 °C primarily relates to morphological changes in the PANI system [30]. The sharp mass loss beginning at about 450 °C presumably corresponds to the large-scale thermal degradation of PANI chains [26]. Gradual weight loss over the wide temperature range could be attributed to the good thermal stability of the PANI main chain.

The conductivity of the PANI is 6.8×10^{-2} S/cm, which is similar to those of the PANI produced by other methods [11,31].

In summary, PANI can be synthesized by water/IL IP. This route has some obvious advantages, such as PANI nanoparticles can be fabricated and both solvents used are environmentally benign. We believe that this strategy can be used to synthesize some other useful polymers.

Acknowledgements

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